

PROCESS FOR PREPARATION OF EPOXYDIPHOSPHONATE

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Abstract of JP 51143620 (A)

PURPOSE: Epoxyester of hypophosphoric acid of formula I (where R is hydrocarbon residue), e.g. diglycidylether of 1-hydroxyethane-1, 1hypophosphoric acid II.

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エポキシジボスホネートの製造法
特許請求の範囲に記載された発明の数 2

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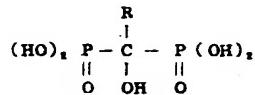
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明細書

発明の名称 エポキシジボスホネートの製造法

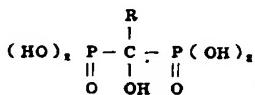
特許請求の範囲

(1) 一般式



(式中Rは炭化水素基を示す)で表わされるジリン酸もしくはその部分中和された酸性塩に、分子中に二個以上のオキシラン基を有するポリエポキシ化合物一種もしくは二種以上を、前記ジリン酸中のPOH基と少なくとも等モル量反応させることを特徴とする、前記一般式で表わされるジリン酸のエポキシエステルの製造法。

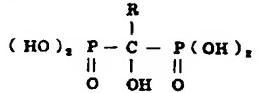
(2) 一般式



(式中Rは炭化水素基を示す)で表わされるジリン酸もしくはその部分中和された酸性塩に、エビハロヒドリンを反応させ、次いで前二者の場合はアルカリ処理を行なうことを特徴とする、前記一般式で表わされるジリン酸のエポキシエステルの製造法。

発明の詳細な説明

本発明は、一般式



(式中Rは炭化水素基を示す)で表わされるジリン酸の新規なエポキシエステルの製造法に関するものである。

接着剤、電気絶縁材料、塗料等の分野ではエポキシ樹脂が広く利用されて優れた性質を示している。しかしながら、これらエポキシ樹脂に対して期待される性能の全てが満足されているわけではない。たとえば電気絶縁材料や塗料、樹脂加工等

の分野では、安全管理の面から難燃化又は不燃化が要求されており、それに応じるためにハログン含有無水カルボン等の硬化剤やアンチモン、ハログン、リン等を含む難燃化剤を用いて改善を計る等の試みがなされているが、反応上添加量に自ら限度があり、必ずしも充分な効果を与えることはできない。また塗料の分野でも、エポキシ系化合物は他に比して比較的接着力が優れているが、防食性や耐久性を付与することは容易ではない。

一方、従来難燃性や防食性が望まれる分野では、種々のリン酸化合物が使用されている。これらは多くはオルソ又はメタリン酸のエステル、つまりホスフェートかホスファイトであり、P-O-C結合、すなわちリン酸エステル結合から成るものである。これらとは別にP-O-C結合に比べて結合エネルギーの大きいP-C結合を有する化合物、たとえばホスホネートは化学的にも熱力学的にも安定性が大きく工業的に優れた性質を有することが期待できるが、ホスホネートは通常グリニヤー反応、不飽和基へのホスフイン、ホスファイトの付

加反応、アルブゾブ反応等で合成しなければならず、反応条件の制約が大きいこと、反応工程が長いこと、反応に使用する各試剤の合成経路が長いこと等のために、製品コストが高く、またより限定した形の化合物しか得られず、広範な用途に適用するまでに到つていないのが現状である。

本発明者らは、安価かつ安定性の高いホスホネートの製造と利用に関して種々研究を重ねた結果、先に酢酸又は塩化アセチルと磷酸又は三塩化リンとの反応で合成される/-ヒドロキシエタン-/-/-ジリン酸が特異的な性能を有していることを知見した。このジリン酸は一般的には金属イオン封鎖剤、洗浄ビルダー、歯磨添加剂、無機スライサー添加剤等としての利用が提案されているが、本発明者らはこのジリン酸は金属に対してキャレート形成反応を行なわせるのに適した骨格を有しております。また各種の化合物と反応して新規なキャレート結合形成能を有する重合性不飽和ジリン酸を合成でき、これらのエポキシジリン酸化合物が、高いP含有量を有するため難燃性を与えやすく、ま

たキャレート結合形成能があることから、水系接着剤、水系塗料、電気絶縁材料等の基材や各種組成物の難燃化剤としても有効であることを見出し、本発明に到達した。

本発明の前記一般式で表わされるジリン酸のエポキシエステルの製造法は、前記一般式で表わされるジリン酸もしくはその部分中和された酸性塩に、分子中に二個以上のオキシラン基を有するポリエポキシ化合物を、前記ジリン酸中のPOH基と少なくとも等モル量反応させて、一個のオキシラン基を附加させ、他のオキシラン基を残留させること、あるいは前記一般式で表わされるジリン酸もしくはその酸性塩にエビハロヒドリンを反応させたちアルカリ処理してオキシラン形成を行なうこと、又は前記式Iで表わされるジリン酸の中性塩にエビハロヒドリンを反応させて脱塩反応させることを含むものである。

本発明に用いられる前記一般式で表わされるジリン酸は、Rがメチル、エチル等の低級アルキル基でも、ステアリル等の高級アルキル基でも、フ

エニル等の環状炭化水素基であつてもよいが、生成物が水性であることを望む場合は、C₆以下が好ましい。たとえば/-ヒドロキシエタン-/-/-ジリン酸、/-ヒドロキシプロパン-/-/-ジリン酸、/-ヒドロキシブタン-/-/-ジリン酸、/-ヒドロキシフェニルメタン-/-/-ジリン酸、/-ヒドロキシステアリルメタン-/-/-ジリン酸等が用いられる。

ポリエポキシ化合物としては、グリシジルエスチル類、グリシジルエーテル類等のグリシジル型エポキシ化合物、エポキシ化ポリオレフィン化合物、エポキシ化動植物油系化合物、環状脂肪族エポキシ化合物等が用いられ、個々の例としては、ジグリシジルエーテル、ブタンジオールジグリシジルエーテル、グリセリントリグリシジルエーテル、ポリエチレングリコールジグリシジルエーテル、ポリブロビレンジグリシジルエーテル、ビスフェノールA-ジグリシジルエーテル、ジベンゼンジオキシド、シクロヘンタンジエンジオキシド、ダイマー酸ジグリシジル、エポキシ化植物油、J.

4-エポキシシクロヘキシル-3, 4-エポキシシクロヘキサンカルボキシレート等があげられる。

前記一般式のジリン酸とポリエポキシ化合物との反応は、ジリン酸ノモルに對しポリエポキシ化合物ノモルもしくはそれ以上を用い、ジリン酸の部分中和された酸性塩たとえばアルカリ金属塩、アンモニウム塩の場合 POH 基ノモルに對しポリエポキシ化合物等モルもしくはそれ以上を用いることが好ましい。反応条件は特に制限されないが、ポリエポキシ化合物にジリン酸もしくはその塩を加えて行なう方式が好ましく、この際、POH 基のモル量よりもポリエポキシ化合物のモル量が少ないときは、重合反応が起こるおそれがあるので注意を要する。反応温度は室温ないし100°Cで、必要によりエポキシ開環反応触媒として有効な化合物、たとえば第三級アミン、第四級アミン、環素錯体、金属錯体等を用いる。特に好ましい触媒としては、トリエチルアミン、トリ-*N*-ブチルアミン、ビリジン、ジメチルアニリン、N,N-ジメチルバタロイジン、トリメチルベンジルアンモ

ニウムクロリド、ドデシルビリジニウムクロリド、三弗化硼素エーテル化物、フェロセン、チタノセン、ジルコノセン、アンモニウムトリスアセチルアセトナート、ジルコニウムテトラキスアセチルアセトナート等があげられる。

本発明に用いらるエピハロヒドリンとしては、たとえばエピクロロヒドリン、エピブロモヒドリン、ハログン化アルコールグリシルエーテルたとえば 1-(1-クロロ-2-ヒドロキシプロポキシ)-ブタン-4-グリシジルエーテル、2-クロロエチル-1-グリシジルエーテルがあげられる。

前記一般式のジリン酸の中性塩たとえばリチウム、ナトリウム、カリウム等のアルカリ金属塩、第三級アミン塩等のアミン塩との反応は、ジリン酸ノモルに對しエピハロヒドリン 2~4 モルを用い脱塩反応を行ないエポキシ化する。また前記一般式のジリン酸もしくはその酸性塩とエピハロヒドリンの反応は、ジリン酸もしくはその酸性塩ノモルに對しエピハロヒドリン 2~4 モルを用いて

付加反応を行ない、次いでアルカリ化合物たとえば水酸化リチウム、水酸化ナトリウム、水酸化カリウム、炭酸ナトリウム、炭酸カリウム、節酸カリウム等で処理してハロヒドリン基を脱塩閉環する。

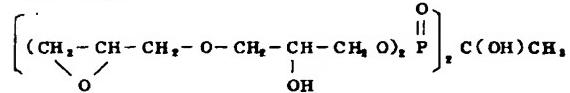
こうして生成される前記一般式のジリン酸のエポキシエステルは、金属に対するキャレート形成能が優れた、難燃化しやすいエポキシ化合物であり、工業的に広い用途が期待される。これらの化合物は、難燃性エポキシ樹脂ベースとし、またキャレート結合形成能のあるエポキシベースとして、接着剤、樹脂、塗料等の分野で有効である。

以下本発明の実施例を示す。例中部及び%は重量基準である。

実施例-1

1-ヒドロキシエタン-1, 1-ジリン酸の60%水溶液 34.3 部にジグリシジルエーテル 53 部を加え、攪拌しつつ 80°C に加温し、30 分後反応を終了した。反応系の pH は反応開始前は 1 以下であり、反応終了後 5.8 の無色透明な粘稠液であつた。反

応生成物を無水硫酸マグネシウムで脱水処理して得た生成物は、元素分析の結果 P 含有量 8.67% (下記式としての計算値 8.93%)、エポキシ当量 173 で、赤外線吸収分析の結果、755 cm⁻¹、1000 cm⁻¹、1040 cm⁻¹、1145 cm⁻¹、1285 cm⁻¹、2950 cm⁻¹、3050 cm⁻¹ に強い赤外線吸収が認められ、下記式の化合物に相当することが認められた。この化合物の 16% の水を含む溶液粘度は 1.8 PS (18°C) であつた。

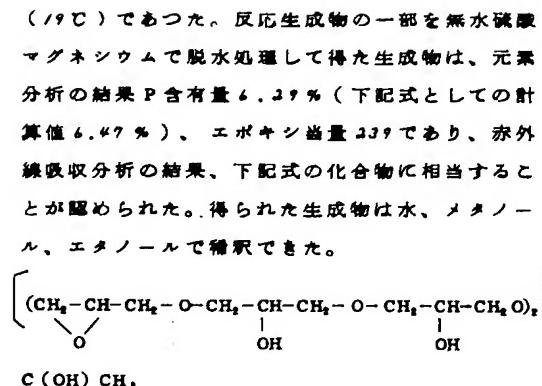


実施例-2

1-ヒドロキシエタン-1, 1-ジリン酸の 60% 水溶液 34.3 部にグリセリンジグリシジルエーテル 1.6 部を加え、これに更に N,N-ジメチルバタロイジン 0.2 部を加えて攪拌しつつ 80°C に加温し、40 分後反応を終了した。反応系の pH は反応開始前は 1 以下であり、反応終了後 4.1 であつた。反応生成物は無色透明であり、粘度は 2.1 PS

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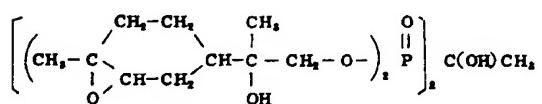
分析の結果 P 含有量 5.78% (下記式としての計算値 6.47%)、エポキシ当量 239 であり、赤外線吸収分析の結果下記式化合物に相当することが認められた。生成物は水、メタノール、エタノールで稀釈できた。



実施例 - 3

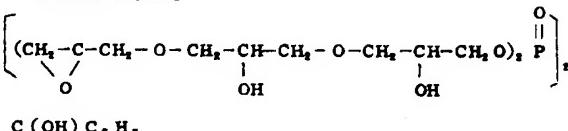
1-ヒドロキシフエニルメタン-1, 1-ジリン酸の40%水溶液 67.0部に、グリセリンジグリジルエーテル 81.6部及びトリメチルベンジルアンモニウムクロリド 0.1部を加えて攪拌し、これを 80°C にて 30 分間加熱反応することにより淡黄色透明液体を得た。反応系の pH は反応前 1 以下であり、反応終了後 5.7 であつた。反応生成物の一部を無水芒硝で脱水処理して得た生成物は、元素

(下記式としての計算値 7.06%)、エポキシ当量 220 であり、赤外線吸収分析の結果反応生成物は主として下記式に相当することが認められた。反応生成物はメタノール、エタノールに易溶性であつた。



実施例 - 4

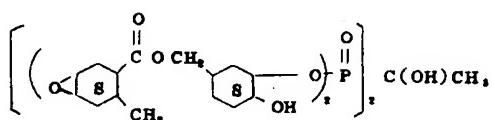
1-ヒドロキシエタン-1, 1-ジリン酸の60%水溶液 34.3部に 3, 4-エポキシ-6-メチルシクロヘキシルメチル-3, 4-エポキシ-6-メチルシクロヘキサンカルボキシレート 1/2部、トリ-エ-ブチルアミン 0.2部を混合し、攪拌しつつ 80°C にて加熱し、50 分間反応を行なつた。反応生成物は淡黄色液体であつた。生成物の一部をベンゼンで共沸脱水したのち過剰のベンゼンを留去し、淡黄色粘稠液体を得た。この液体の粘度は、14.5 PS であつた。脱水精製物の元素分析の結果、P



実施例 - 4

1-ヒドロキシエタン-1, 1-ジリン酸の60%水溶液 34.3部にジベンテンジオキシド 67.2部、トリ-エ-ブチルアミン 0.1部、アルミニウムトリスアセチルアセトナート 0.1部を加え、80°C にて加熱して 40 分間反応を行つた。反応生成物の 1 部を探り無水硫酸マグネシウムで脱水精製して得られた生成物は、淡黄色透明な粘稠液体であり、粘度は 12 PS (20°C) であつた。反応系の pH は反応前 1 以下であり、反応終了後は 6.3 であつた。脱水精製物の元素分析の結果 P 含有量 6.74%

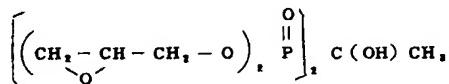
含有量 4.31% (下記分子式としての計算値 4.50%)、エポキシ当量 345 で赤外線吸収分析の結果主として下記に相当することが認められた。



実施例 - 6

1-ヒドロキシエタン-1, 1-ジリン酸の60%水溶液 34.3部に、水酸化ナトリウム 1/6 部を水 34 部に溶解して加えて中和して Na 塩とした。これにエビプロモヒドリン 1/6 部を加えて 70°C で 40 分間反応を行なつて反応を終了した。反応生成物の一部を探り、これに過剰のトルエンを加えて脱水し、更にエビプロモヒドリンを減圧留去し、生成した塩を分別して淡黄色粘稠液体を得た。粘度 13.2 PS (10°C) であつた。この精製物の元素分析を行なつた結果、P 含有量 5.01% (下記式として 5.27%)、エポキシ当量 102 であり、ハロゲン

残留は微量であつた。これらの分析の結果、得られた生成物の構造は下式に相当することが認められた。



実施例-7

1-ヒドロキシエタン-1, 1-ジリン酸の60%水溶液34.3部に、水酸化ナトリウム8部を水17部に溶解して搅拌して加えて中和したのちエビプロモヒドリン28部を加えて80°Cで40分間反応を行なつた。反応液は淡黄色透明であつた。これを30°Cに下げ水酸化ナトリウム8.0部を水17部に溶解して加えて20分間搅拌したのち、更に60~70°Cに加温して40分間反応を行なつた。反応終了後のpHは7.6であつた。反応生成物のエポキシ当量は43.5であり、この反応液40部にトリエチレンテトラミン4部を加えたところ、室温で30分後60°Cに昇温し、淡黄色透明の含水樹脂を与えた。この樹脂はバーナーから外すと直ちに消火し、難燃性であつた。

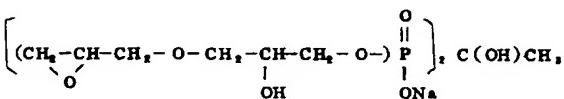
シジボスホネート10部をそれぞれ下記第1表に示されるエポキシ硬化剤により硬化難燃性樹脂を製造した（それぞれ参考例1~4）。得られた樹脂の燃焼性を第1表に示す。

第1表

	硬化剤	硬化時間 (分)	燃焼性
参考例1	ジエチレントリアミン 2部	25	バーナーから外すと直ちに消火
・2	・ 2.5部	20	・
・3	トリエチレンテトラミン 2.5部	15	・
・4	・ 1.5部	20	・

実施例-8

1-ヒドロキシエタン-1, 1-ジリン酸の60%水溶液34.3部に水酸化ナトリウム8部を水17部に溶解して搅拌下に滴下反応させ1-ヒドロキシエタン-1, 1-ジリン酸ナトリウム塩水溶液を得た。これにジグリシジルエーテル26.5部を加え、80°Cで30分間反応して淡黄色透明粘稠液を得た。反応終了時の溶液のpHは6.9であつた。反応生成物の一部を取り脱水精製して得た生成物はPの元素分析の結果、P含有量11.94%（下記式としての計算値12.15%）、赤外線吸収分析の結果下記式に相当することが認められた。生成物は水、メタノールに可溶であり、トリエチレンジアミンで硬化し淡黄色透明の難燃性樹脂を与えた。



参考例-1~4

実施例1~4において合成された新規なエポキ

第2表

材質	養生条件	引張剪断強度(%)
ラワン合板-軟鋼	25°C 34時間、60% pH	113
ラワン合板-ラワン合板	・ ・ ・	121

* 5mm厚、1級

25mm幅×125長さ

出願人代理人 猪股清

参考例-5

実施例-5の生成物15部にヘキサメチレンジアミン3部を加えて充分搅拌し、下記第2表に示す材質での接着試験を行なつた結果、いずれも木破が発生し、良好であつた。また硬化した樹脂はバーナーから外すと直ちに消火し難燃性であつた。

添附書類の目録

(1) 明細書	1通
(2) 横面	1通
(3) 委任状	1通

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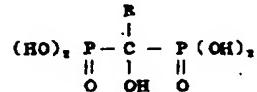
SPECIFICATION

20 TITLE OF THE INVENTION

Process for preparation of epoxydiphosphonate

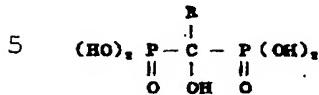
CLAIMS

1. A process for preparing an epoxyester of a diphosphonic acid represented by the following formula:



wherein R represents a hydrocarbon group,
30 the process comprising:
allowing the diphosphonic acid represented by the above formula or a partially neutralized acid salt thereof to react with one or two or more polyepoxy compounds having two or more oxirane groups in the molecular structure in a molar amount at least equivalent to that of the POH group in the phosphonic acid.

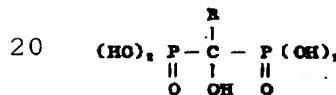
2. A process for preparing an epoxyester of a diphosphonic acid represented by the following formula:



wherein R represents a hydrocarbon group,
 the process comprising:
 allowing the diphosphonic acid represented by the above
 10 formula, an acid salt or a neutral salt thereof to react with
 an epihalohydrin; and
 treating the resulting product with an alkali if one of
 the former two is used.

15 DESCRIPTION OF THE INVENTION

The present invention relates to a process for preparing a novel epoxyester of a diphosphonic acid represented by the following formula:



wherein R represents a hydrocarbon group.

Epoxy resins have been widely used in adhesive agents, electric insulation materials, coatings, and the like, and
 25 exhibit high performance. Epoxy resins, however, fail to satisfy required levels in some properties. For example, for electric insulation materials and coatings, and processing of resins, properties of flame retardance and incombustibility are required for safety. There have been some studies conducted
 30 to satisfy this demand. In these studies, a curing agent such as anhydrous halogen containing-carvone, a flame retardant containing antimony, a halogen, phosphorus, or the like are used to improve the properties. In order to allow the reaction to proceed, these substances cannot be added in amounts over
 35 certain levels, and thereby do not necessarily produce

sufficient effects. When used in a coating, epoxy compounds show relatively excellent adhesivity compared to other materials; however, it is difficult to provide anti-corrodibility and durability to the coating with the epoxy
5 compounds.

In fields in which flame retardance and anti-corrodibility are required, phosphoric acid compounds of various types have been conventionally used. Most of these are esters of ortho- or metaphosphoric acids, that is, phosphates
10 and phosphites, and include a P-O-C bond or a phosphonic acid ester bond. Apart from these compounds, compounds having a P-C bond, which has a higher bond energy than that of the P-O-C bond, such as phosphonates are chemically and thermodynamically stable, and are expected to show industrially favorable
15 performance. Phosphonates are typically synthesized through a reaction such as the Grignard reaction, an addition reaction of a phosphine or phosphite to an unsaturated group, or the Arbuzov reaction. In these reactions, reaction conditions are restricted, the reaction processes requires a long time, and
20 synthesis paths of reagents used in the reaction are long. For these and other reasons, the product cost is high. In addition, products through such a reaction have a configuration of some determined type. Therefore, these compounds have not been widely used.

25 The present inventors studied on preparation and use of inexpensive and stable phosphonate to find specific performance of 1-hydroxyethane-1,1-diphosphonic acid synthesized through the reaction between acetic acid or acetyl chloride, and phosphoric acid or trichlorophosphate. This diphosphonic acid
30 have been typically proposed for use in metal ion blocking agents, detergent builders, additives for dentifrices, additives for inorganic slurries, and the like. The present inventors, however, focused on the characteristics and properties of this diphosphonic acid that this diphosphonic acid has the skeleton capable of easily reacting with a metal
35

to form a chelate, that this diphosphonic acid easily synthesizes novel polymeric unsaturated diphosphoric acids capable of forming a chelate bond with compounds of various types, that these epoxy diphosphoric acid compounds easily 5 provide flame retardance owing to its high P content, and that these epoxy diphosphoric acid compounds are capable of forming a chelate bond. Considering these facts, the present inventors found that these epoxy resin compounds are advantageously used as base materials in aqueous adhesive agents, aqueous coatings, 10 electric insulation materials and the like, and as flame retardants for various compounds. Thus, the present inventors completed the present invention.

The process for preparing an epoxyester of a diphosphonic acid represented by the above formula of the present invention 15 includes a step of allowing a diphosphonic acid represented by the above formula or a partially neutralized acid salt thereof to react with polyepoxy compounds having two or more oxirane groups in the molecular structure in a molar amount at least equivalent to that of the POH group in the phosphoric acid so 20 that one of the oxirane groups is lost by the addition reaction and the other oxirane groups are remained; steps of allowing a diphosphonic acid represented by the above formula or an acid salt thereof to react with an epihalohydrin, and treating the resulting product with an alkali to form an oxirane; or a step 25 of allowing a neutral salt of a diphosphonic acid represented by the above formula I to react with an epihalohydrin so that the desalt reaction occurs.

In diphosphonic acids represented by the above formula used in the present invention, R may be a lower alkyl group such 30 as methyl or ethyl group, a higher alkyl group such as stearyl group, or a cyclic hydrocarbon group such as phenyl group. However, in order to yield an aqueous product, R is preferably a group having not more than eight carbon atoms. Examples thereof include 1-hydroxyethane-1,1-diphosphonic acid, 35 1-hydroxypropane-1,1-diphosphonic acid,

1-hydroxybutane-1,1-diphosphonic acid,
1-hydroxyphenylmethane-1,1-diphosphonic acid, and
1-hydroxystearyl methane-1,1-diphosphonic acid.

Examples of the polyepoxy compounds include glycidyl
5 epoxy compounds such as glycidyl esters and glycidyl ethers,
epoxidized polyolefin compounds, epoxidized animal or
vegetable oils, and alicyclic epoxy compounds. Specific
examples of these include diglycidyl ether, butanediol
diglycidyl ether, glycerin triglycidyl ether, polyethylene
10 glycol diglycidyl ether, polypropylene glycidyl ether,
bisphenol A diglycidyl ether, dipenthen dioxide, cyclopentane
diene dioxide, diglycidyl esters of dimer acids, epoxidized
vegetable oils,
3,4-epoxycyclohexyl-3,4-epoxycyclocarboxylate.

15 In the reaction between a diphosphonic acid represented
by the above formula and polyepoxy compounds, the polyepoxy
compounds are used in an amount of 4 mol or more with respect
to 1 mol of the diphosphonic acid. If a partially neutralized
acid salt such as an alkaline metal salt or an ammonium salt
20 of a diphosphonic acid is used, the polyepoxy compounds are
preferably used in a molar amount equivalent to or more than
that of the POH group. The conditions for the reaction are not
particularly limited, and it is preferable that a diphosphonic
acid or a salt thereof is added to polyepoxy compounds. In this
25 case, if the molar amount of polyepoxy compounds is less than
the molar amount of the POH group, the polymerization reaction
may occur. The reaction temperature is from room temperature
to 100°C. A compound that effectively serves as an
epoxy-ring-opening catalyst such as a tertiary amine,
30 quaternary amine, boron complex, or metal complex may be used,
if necessary. Examples of particularly preferable catalysts
include triethylamine, tri-n-butylamine, pyridine,
dimethylaniline, N,N-dimethyl para-toluidine, trimethyl
benzil ammonium chloride, dodecylpyridinium chloride,
35 trifluoroboron etherate, ferrocene, titanocene, zirconocene,

ammonium tris acetylacetonato, and zirconium tetrakis acetylacetonato.

Examples of epihalohydrins used in the present invention include epichlorohydrin, epibromohydrin, and halogenated alcohol glycidyl ether such as 5 1-(1-chloro-2-hydroxypropoxy)-butane-4-glycidyl ether, and 2-chloroethyl-1-glycidyl ether.

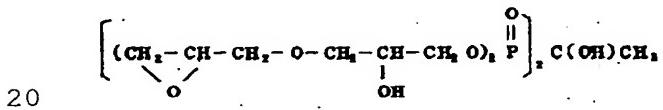
In the reaction involving a neutral salt of a diphosphonic acid represented by the above formula such as a salt with an 10 alkaline metal, for example, lithium, sodium or potassium, or a salt with an amine, for example, a tertiary amine, an epihalohydrin is used in an amount of 2 to 4 mol with respect to 1 mol of the diphosphonic acid to desalt and epoxidize the salt. In the reaction between a diphosphonic acid represented 15 by the above formula or an acid salt thereof and an epihalohydrin, the epihalohydrin is used in an amount of 2 to 4 mol with respect to 1 mol of the diphosphonic acid or the acid salt thereof to allow the addition reaction to occur. Subsequently, the resulting product is treated with an alkaline compound such as 20 lithium hydroxide, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, or potassium acetate so that the halohydrin group is desaltsed and the ring is closed.

Epoxy esters of diphosphonic acids represented by the above formula produced as described above are excellent in 25 ability to form a chelate with a metal, and easily achieve flame retardance. Application of such epoxy esters in wide industrial fields is demanded. These compounds are suitably used as flame retardant epoxy resin base materials or epoxy base materials capable of forming a chelate bond in adhesive agents, 30 resins, coatings, and the like.

Hereinafter, examples of the present invention are described. The units "part" and "%" in examples are based on weight.

35 Example 1

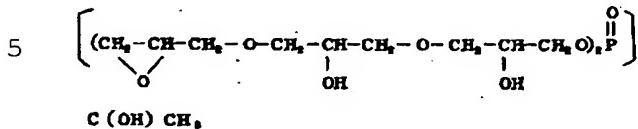
An amount of 53 parts of diglycidyl ether was added to 34.3 parts of 60% aqueous solution of 1-hydroxyethane-1,1-diphosphonic acid, and the mixture was heated to 80°C under stirring. The reaction was terminated 30 minutes later. The pH of the reaction system was not higher than 1 before the reaction, and was 5.8 after the reaction. The reaction product was a hyaline sticky fluid. The reaction product was dehydrated with anhydrite magnesium sulfate to yield a product. The results of the elemental analysis on the product showed that the product had a P content of 8.67% (8.93% calculated based on the following formula), and an epoxy equivalent of 173. The result of the infrared absorption analysis showed that the product intensely absorbed infrared light at 755 cm⁻¹, 1000 cm⁻¹, 1040 cm⁻¹, 1145 cm⁻¹, 1285 cm⁻¹, 2950 cm⁻¹, and 3050 cm⁻¹, and corresponds to the compound represented by the following formula. The viscosity of a 16% aqueous solution of the compound was 18 PS (18°C).



Example 2

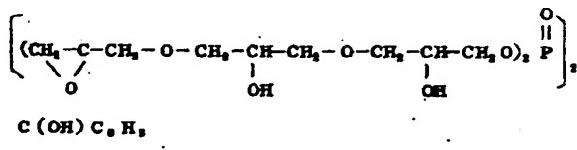
An amount of 81.6 parts of glycerin diglycidyl ether was added to 34.3 parts of 60% aqueous solution of 1-hydroxyethane-1,1-diphosphonic acid, and 0.2 parts of N,N-dimethyl para-toluidine was added to the mixture. The mixture was heated to 80°C under stirring. The reaction was terminated 40 minutes later. The pH of the reaction system was not higher than 1, and was 6.1 after the reaction. The reaction product was hyaline and sticky, and had a viscosity of 21 PS (19°C). Portion of the reaction product was dehydrated with anhydrite magnesium sulfate to provide a product. The results of the elemental analysis on the product showed that the product had a P content of 6.29% (6.47% calculated based on the following formula), and an epoxy equivalent of 239. The infrared

absorption analysis revealed that the product corresponds to the compound represented by the following formula. The obtained product was diluted with water, methanol or ethanol.



Example 3

10 An amount of 81.6 parts of glycerin diglycidyl ether and 0.1 parts of trimethylbenzyl ammonium chloride were added to 67.0 parts of 40% aqueous solution of 1-hydroxyphenylmethane-1,1-diphosphonic acid, and the mixture was stirred. Then, the mixture was allowed to react while being heated to 80°C for 30 minutes to yield a transparent light yellow liquid. The pH of the reaction system was not higher than 1 before the reaction, and was 5.7 after the reaction. Portion of the reaction product was dehydrated with anhydrite sodium sulfate to yield a product. The results of the elemental analysis on the product showed that the product had a P content of 5.78% (6.08 % calculated based on the following formula), and an epoxy equivalent of 225. The infrared absorption analysis revealed that the product corresponds to the compound represented by the following formula. The obtained product was diluted with water, methanol or ethanol.

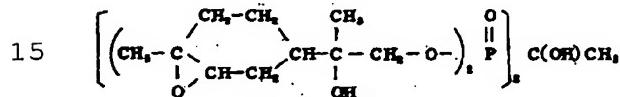


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Example 4

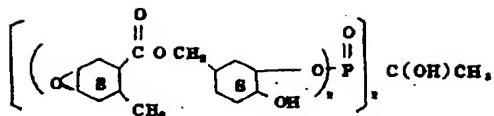
An amount of 67.2 parts of dipenthen dioxide, 0.1 parts of tri-n-butylamine and 0.1 parts of aluminum tris acetylacetonato were added to 34.3 parts of 60% aqueous solution of 1-hydroxyethane-1,1-diphosphonic acid. The mixture was

heated to 80°C, and the reaction was allowed to proceed for 40 minutes. Portion of the reaction product was dehydrated and purified with anhydrite magnesium sulfate to provide a product. The product was a transparent light yellow sticky fluid and had 5 a viscosity of 12 PS (23°C). The pH of the reaction system was not higher than 1, and was 6.3 after the reaction. The results of the elemental analysis on the purified dehydrated product showed that the product had a P content of 6.74% (7.06% calculated based on the following formula), and an epoxy 10 equivalent of 220. The infrared absorption analysis revealed that the reaction product mainly corresponds to the compound represented by the following formula. The obtained product was easily soluble in methanol or ethanol.



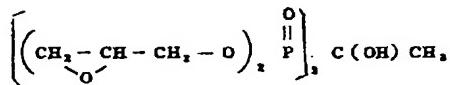
Example 5

An amount of 112 parts of 20 3,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexane carboxylate and 0.2 parts of tri-n-butylamine were added to 34.3 parts of 60% aqueous solution of 1-hydroxyethane-1,1-diphosphonic acid, and the mixture was heated to 80°C under stirring. The reaction was allowed to 25 proceed for 50 minutes. The reaction product was a light yellow liquid. Portion of the product was azeotropically dehydrated with benzene, and excessive benzene was removed to provide a light yellow sticky fluid. The fluid had a viscosity of 14.5 PS. The results of the elemental analysis on the purified 30 dehydrated product showed that the product had a P content of 4.31% (4.50% calculated based on the following formula), and an epoxy equivalent of 345. The infrared absorption analysis revealed that the product mainly corresponds to the compound represented by the following formula.



5 Example 6

An amount of 16 parts of sodium hydride dissolved in 34 parts of water was added to neutralize 34.3 parts of 60% aqueous solution of 1-hydroxyethane-1,1-diphosphonic acid to yield the Na salt. An amount of 83 parts of epibromohydrin was added to 10 the salt, and the reaction was allowed to proceed at 70°C for 40 minutes, and then terminated. Portion of the reaction product was dehydrated with toluene, and epibromohydrin in the product was removed in vacuo to provide the salt. The obtained salt was filtered off to provide a light yellow sticky fluid. 15 The fluid had a viscosity of 13.2 PS (18°C). The results of the elemental analysis on the purified product showed that the product had a P content of 15.01% (15.27% calculated based on the following formula), and an epoxy equivalent of 102. Only 20 a slight amount of the halogen was remained therein. The analysis revealed that the structure of the product corresponds to the following formula.



25

Example 7

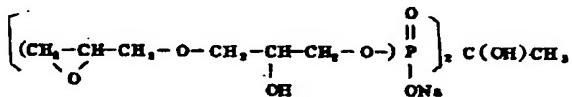
An amount of 8 parts of sodium hydride dissolved in 17 parts of water was added to neutralize 34.3 parts of 60% aqueous solution of 1-hydroxyethane-1,1-diphosphonic acid. 30 Thereafter, 28 parts of epibromohydrin was added thereto, and the reaction was allowed to proceed at 80°C for 40 minutes. The reaction liquid was cooled to 30°C, and 8.0 parts of sodium hydride dissolved in 17 parts of water was added to the reaction liquid, 35 and the resulting mixture was stirred for 20 minutes. The

mixture was further heated to a temperature of 60°C to 70°C, and the reaction was allowed to proceed for 40 minutes. The pH after the reaction was 7.6. The reaction product had an epoxy equivalent of 43.5. An amount of 40 parts of triethylene tetramine was added to 40 parts of the reaction liquid, and the mixture was allowed to stand at room temperature for 30 minutes, and then heated to 60°C to yield a hydrated transparent light yellow resin. Fire disappeared immediately after the resin was removed from a burner, indicating that the resin was flame retardant.

Example 8

An amount of 8 parts of sodium hydride dissolved in 17 parts of water was dropwise added to 34.3 parts of 60% aqueous solution of 1-hydroxyethane-1,1-diphosphonic acid under stirring to allow the reaction to proceed. Thus, an aqueous solution of the 1-hydroxyethane-1,1-diphosphonic acid disodium salt was obtained. An amount of 26.5 parts of diglycidyl ether was added thereto, and the reaction was allowed to proceed at 80°C for 50 minutes to yield a transparent light yellow sticky fluid. The pH of the solution was 6.9 after the reaction. Portion of the reaction fluid was dehydrated and purified. The results of the elemental analysis on the purified dehydrated product showed that the product had a P content of 11.94% (12.15% calculated based on the following formula). The infrared absorption analysis revealed that the product corresponds to the following formula. The product was soluble in water and ethanol, and cured with triethylenediamine to provide a transparent light yellow flame retardant resin.

30



Reference examples 1 to 4

An amount of 10 part of each of the novel epoxy

diphosphonates prepared in Examples 1 to 4 was cured with the epoxy curing agent shown in Table 1 to provide cured flame retardant resins (each assigned to Reference examples 1 to 4). Table 1 shows the flame retardance of the obtained resins.

5

Table 1

	Curing agent	Curing time (min)	Incombustibility
Reference example 1	Diethylenetriamine 2 parts	25	Fire disappeared immediately after removal from a burner.
Reference example 2	Diethylenetriamine 2.5 parts	20	Fire disappeared immediately after removal from a burner.
Reference example 3	Triethylenetetramine 2.5 parts	15	Fire disappeared immediately after removal from a burner.
Reference example 4	Triethylenetetramine 1.5 parts	20	Fire disappeared immediately after removal from a burner.

Reference example 5

An amount of 3 parts of hexamethylenediamine was added
10 to 15 parts of the product obtained in Example 5, and the resulting mixture was sufficiently stirred. An adhesion test was performed using the materials shown in Table 2. Favorable results were obtained in either case, that is, the wood materials were broken. Fire disappeared immediately after the
15 cured resin was removed from the burner, indicating that the cured resin was flame retardant.

Table 2

Material	Curing condition	Tensile strength, shear strength (kg/cm ²)
Lauan plywood*-soft steel	25°C, 24 hours, 60% pH	115
Lauan plywood-lauan plywood	Same as above	121

*Thickness: 5mm, First grade

25 mm width x 125 length